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**A Study of the System Ammonia-
Water as a Basis for a Theory
of the Solution of Gases
in Liquids**

EXCHANGE
JUL 24 1921

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHN HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
BENJAMIN SIMON NEUHAUSEN

BALTIMORE
June, 1921

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A STUDY OF THE SYSTEM AMMONIA-WATER AS A BASIS FOR A THEORY OF THE SOLUTION OF GASES IN LIQUIDS

Introduction

To a great extent the aim of most investigations on the absorption of gases in water and other liquids has been to note how far the particular gas conformed with, or deviated from Henry's law. The investigation of the absorption of gases by liquids may be said to begin with Henry's¹ study of the absorption of carbon dioxide by water, a result of which was his famous law that the quantity of a gas absorbed in a liquid is proportional to the pressure of the gas. Dalton's theoretical explanation of this law on the basis of Boyle's law, and his equally well known law of partial pressures of gases² tended to give a very definite trend to the problem of absorption of gases by liquids.

Through the investigations of Bunsen³ on the absorption of the fixed gases, of Schonfeld⁴ on hydrogen sulphide, of Roscoe and Dittmar⁵ on ammonia and hydrochloric acid, and of Sims⁶ on ammonia and sulphur dioxide, it became evident that Bunsen was correct in his stand that the general law that expresses the relation between pressure and the quantity of gas absorbed is a complex function and that conformity to Henry's law in case of the relatively soluble gases was the exception rather than the rule. It was also recognized that the chemical properties of the molecules involved, as for instance their attraction for one another influenced markedly the absorption.

¹ Phil. Trans., 1803; Gilb. Ann., 20, 147 (1805).

² Gilb. Ann., 12, 385 (1803).

³ Liebig's Ann., 93, 1 (1855).

⁴ Ibid., 95, 1 (1855).

⁵ Ibid., 112, 327 (1859).

⁶ Ibid., 118, 333 (1861).

Thus, for example, Roscoe and Dittmar differentiate clearly in their investigation between the absorption of hydrochloric acid gas and ammonia, since a current of air passed through an aqueous solution of hydrochloric acid can only remove gas up to a definite concentration while all the ammonia may be removed from an ammonia solution. This tendency to account for absorption of gases on the basis of physical and chemical properties had its first advocate in Th. Graham¹ who in a very remarkable paper advanced the theory that gases were actually condensed when they were absorbed by a liquid, and that solutions of gases should be considered as binary liquid mixtures of the solvent and liquefied gas. To this view we shall return in the discussion of the results.

The interest as to the validity of Henry's law did not cease, and a number of investigations on the solubility of carbon dioxide were pursued. While Khanikoff and Louguinine² found that Henry's law held up to four atmospheres, v. Wroblewski,³ Cassuto,⁴ and Sander⁵ found that there was a marked deviation up to 100 C.

Ammonia was chosen for the present investigation for a number of reasons. First, it has a very high solubility in water that changes very markedly with the pressure, and thus there are avoided those slight absolute changes in solubility in the case of a gas as carbon dioxide, in the interpretation of which free rein is given to preconceived notions. Secondly, because of its economic importance, the physical constants of ammonia, such as vapor tensions, density of the liquid, surface tension, etc., have been determined more accurately than most other gases. Thirdly, it has a relatively high critical temperature.

The first investigator to work extensively on the absorp-

¹ *Annals of Philosophy*, 12, 69-74 (1826); *Chemical and Physical Researches* (Edinburgh, 1876), pp. 1-6.

² *Ann. Chim. Phys.*, (4), 11, 412 (1867).

³ *Wied. Ann.*, 17, 103 (1882); 18, 290 (1883).

⁴ *Nuovo Cimento*, (5), 6, (1903).

⁵ *Zeit. phys. Chem.*, 78, 513 (1912).

tion of ammonia was Carius.¹ His methods and results were proved unreliable by Roscoe and Dittmar² who investigated the absorption of ammonia by water up to a pressure of 2000 millimetres, at 0° C. Sims³ checked their values and investigated the absorption also at 20° C and 40° C up to 2100 millimetres, and at 100° C up to 1400 millimetres. Watts⁴ also obtained results in agreement with Sims, while Raoult⁵ who worked at one atmosphere and varying temperatures obtained somewhat higher values than the other investigators. Perman⁶ who worked at 0° C, 20° C, and 40° C, with solutions up to 22.5% obtained vapor pressures that tally fairly well with those of Sims. Mallet⁷ working at a pressure of 743–744.5 millimetres obtained the solubilities at –10° C, –20° C, –30° C, and –40° C.

I. The Investigation of the Vapor Phase.

1. Apparatus

The composition of the vapor phase of binary liquid mixtures has been studied both by dynamic and static methods. The principal dynamic method was to allow the liquid mixture to boil at certain pressures and temperatures and to analyze the distillate and residue by a refractometer, as for example, in the classical researches of Zawidzki;⁸ or to bubble air through the solution and absorb the vapors in suitable solutions, and thus determine the composition of the vapors, as was done, for instance, by Perman⁹ in his research on the vapor pressures of ammonia solutions. Both of these dynamic methods are open to rather grave objections. First, in order to have the vapor, collected as distillate or in suitable solutions, correspond with any degree of accuracy to the solution of the composition

¹ Liebig's Ann., 99, 129 (1856).

² Loc. cit.

³ Loc. cit.

⁴ Liebig's Ann. Suppl., 3, 227 (1864).

⁵ Ann. Chim. Phys., (5), 1, 262 (1874).

⁶ Jour. Chem. Soc., 79, 718 (1901); 83, 1168 (1903).

⁷ Am. Chem. Jour., 19, 804 (1897).

⁸ Zeit. phys. Chem., 35, 129 (1900).

⁹ Jour. Chem. Soc., 83, 1168 (1903).

at the beginning or the end of the experiment, one has to begin with a large volume of liquid; and moreover one must distill off only a small portion. Especially in cases in which one of the components has a high vapor pressure, the process should be continued for only a short time. It is very questionable, as Roozeboom¹ observes, whether in mixtures, in which there is a great difference in the composition of both phases, whether the vapor that is formed at the first few minutes corresponds to the true equilibrium. In fact, impelled by such considerations, Cunaeus² preferred to let the vapor remain in contact with the liquid and analyzed the same by optical methods. Moreover, as in the present investigation, solutions of high concentrations of ammonia were used, and the total vapor pressure of the solution is most often more than one atmosphere even at 0° C, distillation consequently was made rather difficult. As for the bubbling method, its disadvantages have already been expressed by Perman:³ "Unfortunately, the method is not applicable over a very wide range of temperature or with very varying concentrations of the solution, for when the vapor pressure becomes nearly equal to atmospheric pressure, a very little air will draw off a large quantity of vapor, and moreover evaporation of ammonia becomes so rapid, that it is impossible to keep the temperature constant." Another obstacle to the use of any dynamic method for this investigation, can be seen from one of the results obtained at 0° C. An ammonia solution which has a partial pressure of 1868 mm ammonia at 0° C, has a partial pressure of 0.51 mm of water. Now assuming ammonia to obey the ideal gas laws, to obtain even 5 mg of water, 22.8 litres of vapor reduced to standard conditions, or practically one gram mole of ammonia would have to be distilled off, a volume too large to deal with, and moreover, a huge quantity of solution would be required in order to be able to neglect the loss of that much ammonia.

¹ Heterogene Gleichgewichte, II, part I, page 20.

² Zeit. phys. Chem., 36, 232 (1901).

³ Loc. cit.

A static method for measuring partial pressures was therefore developed on the basis of the following considerations.

At a fixed temperature, a solution of a certain definite composition of A and B, has a fixed total pressure, made up of two well defined partial pressures of the vapors of A and B. B is assumed to have a greater vapor pressure than A. Now, suppose that by some means a quantity of vapor of A is forced into the vapor phase of the system. Since the partial pressure for A is exceeded, some of it will condense. As some of the vapor of B will also dissolve in this condensate, a readjustment will take place, and a solution will be obtained which is somewhat less concentrated with respect to B, and since B has been assumed to have a much greater pressure than A (in the present case, on the order of the relative vapor pressures of ammonia and water), the partial pressure of B is appreciably diminished, while that of A is slightly increased. The system therefore will suffer a lowering in the total pressure, since the volume is not changed appreciably by the minute quantity of condensate.

This idea was then extended as follows: If to ammonia gas at a certain temperature and pressure below that corresponding to the vapor tension of liquid ammonia at that temperature, there is gradually added some water vapor, the pressure of the mixture will rise until the partial pressure of the water vapor equals that corresponding to the partial pressure of water vapor over a solution whose partial pressure of ammonia at that temperature is such as at the start. Any further addition of water vapor will entail condensation of water with consequent solution of some ammonia and reduction in the total pressure.

In Fig. 1 is given a sketch of the apparatus employed. By opening reducing valves R_1 , R_2 , R_3 , and R_4 , ammonia passed in from the ammonia tank into the manometer and small wrought iron tanks T_1 and T_2 . The auxiliary manometer (A M) was bent at an obtuse angle of 157 degrees so that angle "a" had a sine of .1994. Thus a rise or drop of one

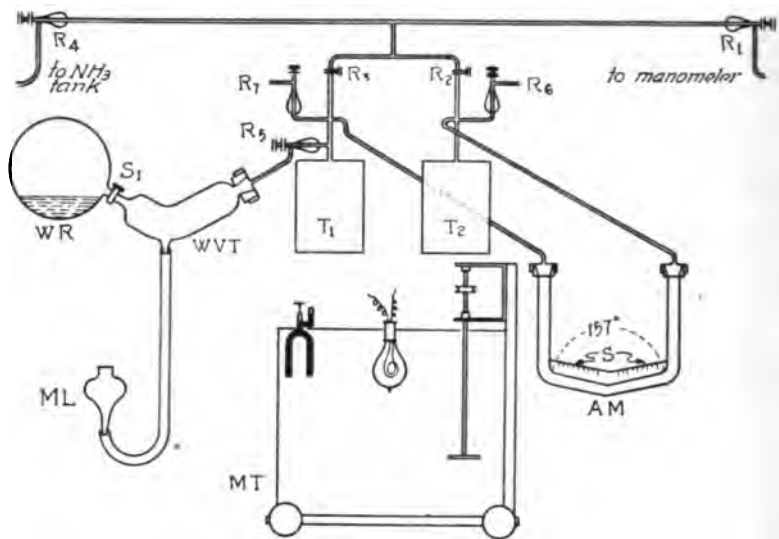


Fig. 1

millimetre in the vertical would be indicated by a rise or drop of five millimetres of the mercury in the oblique tubing and could be read on the attached scale "S" to within 0.2 mm. In other words, change of pressure in tank T_1 , from that of tank T_2 could be measured to 0.08 mm. When we consider that Perman¹ only claimed an accuracy of 0.5 mm for his measurements of the partial pressure of water vapor in total pressures up to 600 mm, the advantage of this static method can be seen.

The water vapor was injected by means of the water vapor injector (W V I) which was connected by means of valve R_5 to T_1 . The distilled water contained in the reservoir bulb (W R) was allowed to distill over into W V I which was evacuated in the following manner. Valves R_2 and R_3 were closed to prevent any direct communication between T_1 and T_2 , while R_1 was opened. Exhaust valves R_6 and R_7 were connected by a "Y" tube to a vacuum pump and evacuated. That was continued intermittently for several hours while

¹ Loc. cit.

S_1 was shut and opened at intervals. R_5 and S_1 were then shut off, and ammonia was passed into T_1 and T_2 through R_2 and R_3 and these tanks were then evacuated. This process was repeated a number of times in order to remove any water vapor remaining in T_1 . By opening R_5 and raising the mercury level bulb (M L) the vapor could be forced into T_1 .

M T was a movable thermostat that could be raised and lowered by means of pulley and tackle. The temperature was regulated to 0.05°C . It was necessary to have this movable thermostat in order to be able to remove it, when the ammonia in T_1 and T_2 had to be cooled by means of a mixture of carbon dioxide snow and ether before the water vapor could be forced in.

All the tubing used in the apparatus was made of brass. The metal-glass joint between the water vapor injector and R_5 is described further in this account.

The pressure was measured by means of a continuous open mercury manometer, which consisted of four glass U-tubes, each having a length of 1600 mm. These were of hard glass with a 6-mm bore and a wall thickness of 1 mm. It is diagrammatically represented in Fig. 2. The structure

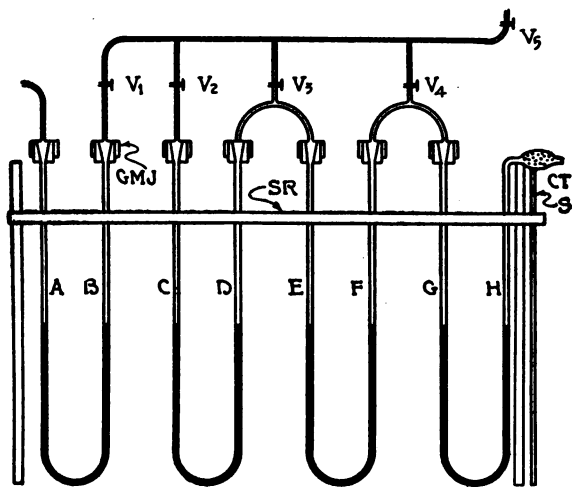


Fig. 2

into which the glass U-tubes were mounted was made of brass tubing, and the glass tubes were connected to it by means of glass-metal joints (G M J) described below. The U-tubes were filled half their length with redistilled mercury, and all the space from the top of the mercury in "B" to the mercury in "G," including the metal structure, was filled with benzene, which was used as the communicating liquid. "H" communicated with the air through a tube filled with soda lime. Since each tube was 1600 mm in length, a total pressure of 8 atmospheres, after making various corrections, plus the corrected barometric reading at the time, could be measured, or approximately 9 atmospheres. Readings were made to the nearest millimetre, so that the maximum error in reading, when all the U-tubes were in series, could be about 4 mm, and there was correspondingly less error as fewer tubes were read. A sliding rod "S R" that could slide over two fixed posts was used to read differences in level between the mercury columns. As can be seen from the diagram, there was no need for correction for meniscus depression. Valves V_1 and V_2 were always open. By keeping valves V_3 and V_4 closed the pressure was measured by the whole series. By opening V_3 the second U-tube was by-passed and by opening both V_3 and V_4 both the second and third U-tubes were by-passed. V_5 was used as an exhaust valve.

The idea of a continuous manometer was first applied by Richards in 1845. Thiesen¹ and then Wiebe² both discussed and described such manometers. By using compressed gas as the communicating fluid, H. Kamerlingh Onnes³ had found such an arrangement very satisfactory in making high pressure measurements, in which greater accuracy was desired than is obtainable with a closed gas manometer. Recently at the Bureau of Standards,⁴ such a manometer was used to measure pressures up to 15 atmospheres with success,

¹ Zeit. Instrumentenkunde, 1881, p. 114.

² Zeit. comprimerte Gase, 1897-1898, pp. 8, 25, 81, 107.

³ Communications Phys. Lab. Leyden, Nos. 44, 67, 70 and 146.

⁴ Jour. Am. Chem. Soc., 42, 206 (1920).

alcohol being used as the communicating liquid. The improvement made in the manometer used in the present work was that the U-tubes were all of practically like bore, and so pressure could be read at any point desired, while in those used at Leyden and at the Bureau of Standards, the tubes were of very small bore with the exception of a small section in the lower part of the left arm and in the upper part of the right arm. Because of this restriction there was much additional manipulation and balancing necessary, and pressures less than a given pressure could not be measured. While the arrangement used in this investigation required a greater quantity of mercury, yet this disadvantage was thought to be overbalanced by the considerations noted above.

Fig. 3 illustrates the method employed in making glass-metal joints. The tubing which it was desired to connect had a flange in it (F). There was a leather gasket on this flange (L_1). The glass tubing was flared and inserted in the metal collar (M C) and made fast with plaster of Paris, (P P). The glass surface was then polished in turn with rough and fine emery and rouge. A second leather gasket (L_2) was put between the collar and the flange, and the two were put firmly together by means of the nut (N) that slipped over the flange and screwed over the collar.

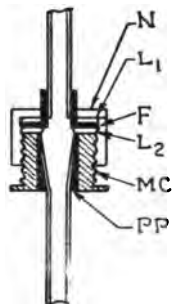


Fig. 3

The ammonia used in this work was obtained from the Goetz Ice Machine Co., Philadelphia, Pa., and was kept over metallic sodium to remove the water. The hydrogen that was generated was allowed to escape by allowing a quantity of ammonia to escape twice daily for a week, until absence of fixed gases was indicated by the fact that no gas remained behind after passing 500 cc of the gas through sulphuric acid. The ammonia which was to be used in the investigation of the vapor phase was then distilled into a second cylinder, the first and last fractions being discarded. In the experiments

on the solubility of ammonia, it was found unnecessary to make this distillation, since the ammonia so dried, showed no trace of fixed gases, and since before starting a run a large volume of ammonia was always run through the apparatus to remove any air.

The temperature of 0°C was obtained by mixing washed ice shavings with water; and those of 20°C and 40°C by means of an electric thermostat.

2. Procedure

In the investigation of the vapor phase, the following procedure was followed. Valves R_1 , R_2 , and R_3 were opened, and a vacuum pump connected with R_6 and R_7 . After the system had been exhausted, R_6 and R_7 were shut off, and R_4 was gradually opened until there was a pressure of about two atmospheres of ammonia in the tanks. Valve R_4 was then shut off and the system again evacuated. This was repeated from six to ten times before every run. Ammonia was then allowed to come into the system. After standing in the thermostat for about half an hour, after which time the manometer did not indicate any change in the pressure, valves R_1 , R_2 , and R_3 were shut off. The continuous manometer as well as the barometer were then read and the temperature of the room was then noted. The thermostat was then lowered, and moved from under the tanks T_1 and T_2 , and T_1 and T_2 were immersed in a mixture of carbon dioxide snow and ether, the ammonia in the tanks being cooled and the pressure reduced to 70–80 mm. The mercury level bulb was then raised and R_5 opened and a quantity of water vapor forced in. R_5 was then closed and T_1 and T_2 were immersed in a beaker of water of 60°C for about ten minutes, and then the thermostat was raised in place. After a half hour when the auxiliary manometer showed no further change in the drop of the mercury on the side connected to T_1 , the drop was noted. This injection of the water was repeated from five to six times until the mercury in this side began to rise, indicating a drop in

pressure in T_1 . The average between the last reading at which an increase in pressure was indicated and the first at which a decrease was noted, was considered as the partial pressure of the water vapor corresponding to that pressure of ammonia at the temperature of the thermostat. The data thus obtained were recalculated as shown in the following specimen record sheet:

Temperature of Bath: 20° C.

Height of mercury in B	1053 mm	
Height of mercury in A	213 mm	840 mm
Height of mercury in D	1049 mm	
Height of mercury in C	205 mm	844 mm
Height of mercury in F	1051 mm	
Height of mercury in E	213 mm	838 mm
Height of mercury in H	1102 mm	
Height of mercury in G	268 mm	834 mm
Total mercury height in manometer		3356 mm
Room temperature near manometer	23.75 C	
Factor to correct for expansion of Hg	0.9956	
Therefore true height mercury column		3341.1 mm
Corrected barometric reading		757.3 mm
Therefore total corrected pressure of mercury		4098.4 mm (R_1)
Length of benzene column in "B"		617 mm (L_1)
Difference in length between benzene in C and D		939 mm (L_2)
Difference in length between benzene in E and F		838 mm (L_3)
Length of benzene column in G		1037 mm (L_4)
Equivalence factor of benzene at 23.75 C to mercury at 0 C is		0.0643 (c)
($L_2 + L_3 + L_4 - L_1$) c		159.1 mm (R_2)
R_1 minus R_2 net ammonia pressure		3939.3 mm
Reading on differential manometer		8.25 mm (max.)
Reading on differential manometer	7.25 mm (first drop)

$$\frac{8.25 + 7.25}{2} \times \frac{2}{5} = 3.1 \text{ mm partial pressure of water.}$$

8. Results

The results obtained are given in the following table:

TABLE I

Composition of the Vapor Phase of Aqueous Ammonia Solutions.
Temperature 0° C

Partial pressure of ammonia in mm	Partial pressure of water in mm
1062	1.04
1100	1.00
1334	0.84
1868	0.51
2078	0.35

Temperature 20° C

Partial pressure of ammonia in mm	Partial pressure of water in mm
1146	8.6
1288	8.3
1445	7.4
2113	5.9
2112	6.0
2647	4.5
2624	4.6
3563	3.7
3725	3.4
3942	3.1

Temperature 40° C

Partial pressure of ammonia in mm	Partial pressure of water in mm
1120	32.1
1389	29.8
1579	26.5
1582	26.4
1926	22.4
2132	20.8
2381	19.3
2546	18.9
2969	18.3
3053	18.3
3395	17.8
3957	17.4
3928	17.4

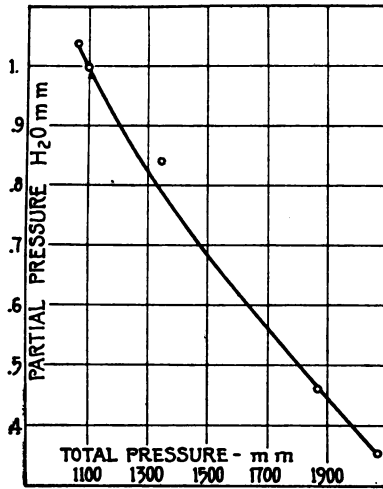


Fig. 4

Partial Pressure H₂O and Total Pressure
NH₃-H₂O System at 0° C

In Figs. 4 and 5 are plotted the partial pressures of water as ordinates and the total pressures of ammonia plus water as abscissae for 0° C, 20° C, and 40° C.

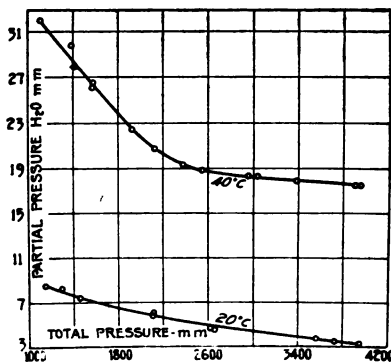


Fig. 5

Partial Pressure H₂O and Total Pressure
NH₃-H₂O System at 20° C and 40° C

II. Investigation of the Liquid Phase.

1. Apparatus

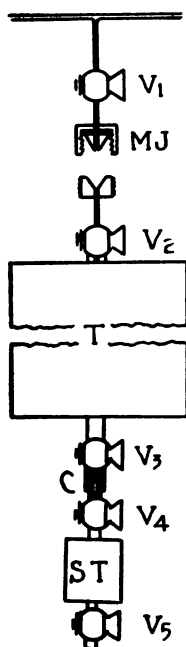


Fig. 6

In Fig. 6 is a sketch of the apparatus for determining the solubility of ammonia in water at different pressures at 0°C , 20°C , and 40°C .

T, the solubility tank of about 500 cc in capacity, was connected to the ammonia tank and to the manometer by means of the metal joint (M J), which as can be seen from the figure was similar in construction to the glass-metal joints. When it was desired to pass ammonia in or to measure the pressure of the gas phase, the connection by means of M J would be made, and valves V_1 and V_2 opened. A sample of the solution could be obtained in the small tank S T which unscrewed from T at C. An eccentric was used to shake the solution by causing the tank to make a 60-degree arc of a circle in the thermostat.

The temperature was regulated to 0.05°C .

The pressure was measured on the same manometer described above.

2. Procedure

The tank T, without the sample tank S T, was filled with water and connected to the cylinder of purified ammonia. By opening V_3 about 300 cc of water was displaced, and about 200 cc of water with an atmosphere of ammonia remained. The sample tank was now screwed on to T, V_3 , V_4 , and V_5 remaining shut and ammonia was allowed to pass in for ten minutes. The tank was then disconnected and shaken for about ten minutes, and then more ammonia was passed in. When, after this procedure had been repeated for a number of hours, the pressure reading reached a value about that desired;

no more ammonia was passed in, and shaking was continued for fifteen minutes at intervals, until pressure readings changed by only several millimetres, and equilibrium was then considered to have been reached. The pressure registered by the manometer, the barometer reading, and the temperature of the room were noted. V_5 was then connected to a vacuum pump, and V_4 and V_5 opened, and S T evacuated. V_5 was then closed and V_3 opened. The pressure above faced the solution into S T. After about a minute V_3 and V_4 were shut and S T unscrewed.

The above method of drawing off a sample was found not to affect the concentration of the solution by the increase of the vapor phase during the short time that the sample was withdrawn. For example, a second sample taken ten minutes later weighed only 8 mg more, and on analysis contained 1/10 of 1% less ammonia than the first sample. This method, moreover, had the advantage that equilibrium did not have to be reached through a small opening in the valve.

The sample tank was carefully dried with filter paper and weighed. The solution was then run into a measured quantity of standard sulphuric acid, the sample tank being thoroughly washed out. S T was dried by compressed air and weighed. Every third or fourth time, it was filled with mercury and weighed to determine the internal volume, so as to ascertain whether any change had taken place because of corrosion.

An aliquot part of the sulphuric acid solution was titrated with dilute sodium hydroxide solution, methyl red being used as the indicator. Thus the quantity of ammonia present was determined.

A sample record sheet of one solubility determination will illustrate the procedure:

Temperature of bath:	20° C	
Height of mercury in B	727 mm	
Height of mercury in A	529 mm	198 mm
Height of mercury in H	767 mm	
Height of mercury in G	571 mm	196 mm

Total mercury height in manometer	394 mm
Room temperature near manometer	28 C
Factor to correct for expansion of mercury	0.9948
Therefore true height of mercury column	392 mm
Correct barometric reading	765 mm
<hr/>	
Total corrected mercury height	1157 mm (R_1)
Difference in columns of benzene between G and B	156 mm (L)
Equivalence factor of benzene at 28° C to mercury at 0° C	0.0638 (c)
$L \times c = R_2$	10 mm
$R_1 - R_2 =$ Total vapor pressure of solution	1147 mm
Weight of sample tank and solution	196.001 g
Weight of sample tank	186.195 g
<hr/>	
Weight of solution	9.806 g
222.91 cc 1.0532 N H_2SO_4 neutralized	3.991 g NH_3
Water present in sample	5.815 g
Therefore 0.686 g NH_3 per gram water	
Weight sample tank and mercury at 24° C	339.835 g
Weight sample tank	186.195 g
<hr/>	
Weight of mercury at 24° C	153.640 g
Therefore volume	11.35 cc
Therefore density of solution	0.864

Now by calculating from Berthoud's¹ values, the density of liquid ammonia at 0° C, 20° C, and 40° C, and from the density of water at these temperatures, there could be obtained the densities that the ammonia solutions would have if no contraction in volume of the water and ammonia had taken place. From these calculated values and densities found for the solutions, the contraction in volume could be calculated. Also, by means of curves in Figs. 4 and 5, the partial pressures of water vapor in the total pressures observed could be read off.

3. Results

In Table II the solubility data obtained is summarized.

Because of the very large difference in the vapor pressures of ammonia and water, it was impossible to plot the partial pressure curves of both the ammonia and water on one diagram. To be able to compare the relative trend of the two curves

¹ Helv. Chim. Acta, **1**, 84-87 (1918).

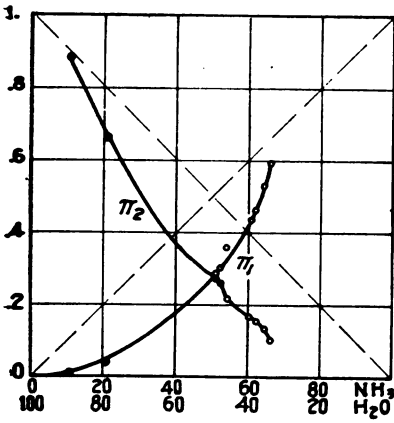


Fig. 7

Reduced Partial Pressure Curves of
NH₃ and H₂O at 0° C

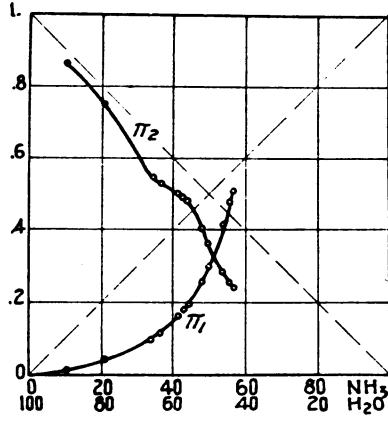


Fig. 8

Reduced Partial Pressure Curves of
NH₃ and H₂O at 20° C

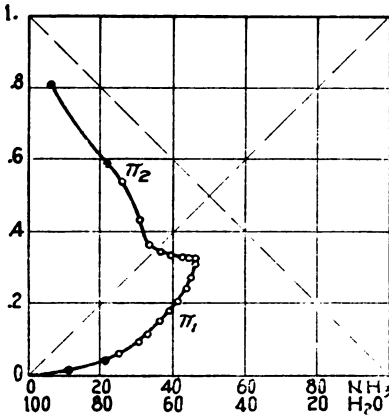


Fig. 9

Reduced Partial Pressure Curves of
NH₃ and H₂O at 40° C

in one diagram, there have been plotted in Figs. 7, 8, and 9, the partial reduced pressures of the ammonia and water, for the various mole fractions of ammonia at 0° C, 20° C, and 40° C. The reduced partial pressures are the ratios between the observed partial pressures and the pressures of the pure components at these temperatures. π_1 and π_2 indicate the ammonia and water curves, respectively. Points marked with an X are taken from Perman's work.

TABLE II
Solubility of Ammonia in Water

Temp. C.	Mole fraction % ammonia	Partial pressure of ammonia, mm	Calc. P. P. NH_3 by Raoult's Law	Partial pressure of water in mm	Calc. P. P. H_2O by Raoult's Law	Density solution	% Contraction in volume	K_1	K_2	K_3
0° C.	51.676	915	1664.5	1.25	2.208	0.842	7.50	1.1032	.5644	.4621
	52.382	944	1687.2	1.19	2.176	0.842	7.80	1.0002	.5547	.4543
	54.735	1140	1763.0	.97	2.068	0.833	7.80	1.0029	.4803	.3897
	61.206	1409	1971.4	.77	1.773	0.817	9.21	1.0582	.4345	.3470
	62.765	1499	2021.6	.708	1.701	0.812	8.52	1.0613	.4184	.3326
	65.076	1684	2096.1	.61	1.600	0.803	8.51	1.0451	.3465	.3041
	65.711	1732	2116.5	.545	1.567	0.800	8.35	1.0456	.3798	.2978
	66.621	1865	2145.9	.46	1.525	0.795	8.12	1.0106	.3572	.2785
	34.886	728	2242.6	9.4	11.304	0.882	7.07	0.6950	.4792	.4073
	36.508	798	2347.	9.25	11.025	0.878	7.25	0.6861	.4575	.3872
20°	42.077	1140	2705.	8.6	10.057	0.864	8.30	0.6017	.3691	.3084
	42.392	1165	2725.1	8.55	10.003	0.862	8.17	0.5965	.3636	.3031
	43.086	1226	2769.8	8.4	9.882	0.854	8.16	0.5832	.3515	.2905

TABLE II (Continued)

20° C																				
	43.731	1281	2811.2	8.3	9.770	0.848	7.37	0.5730	.3414	.2802	43.731	1281	2811.2	8.3	9.770	0.848	7.37	0.5730	.3414	.2802
	48.175	1677	3097.	7.05	8.839	0.845	8.96	0.5239	.2874	.2355	48.175	1677	3097.	7.05	8.839	0.845	8.96	0.5239	.2874	.2355
	49.941	1938	3213.4	6.33	8.692	0.835	8.36	0.4871	.2577	.2092	49.941	1938	3213.4	6.33	8.692	0.835	8.36	0.4871	.2577	.2092
	53.940	2655	3467.5	5.1	7.997	0.825	9.47	0.4166	.2032	.1632	53.940	2655	3467.5	5.1	7.997	0.825	9.47	0.4166	.2032	.1632
	55.970	3076	3598.	4.45	7.645	0.817	9.47	0.3903	.1819	.1449	55.970	3076	3598.	4.45	7.645	0.817	9.47	0.3903	.1819	.1449
	56.923	3277	3659.3	4.15	7.476	0.815	9.65	0.3808	.1737	.1381	56.923	3277	3659.3	4.15	7.476	0.815	9.65	0.3808	.1737	.1381
40° C	25.011	752	2915.6	36.5	41.143	0.902	6.05	0.4192	.3328	.2875	25.011	752	2915.6	36.5	41.143	0.902	6.05	0.4192	.3328	.2875
	25.366	774	2957.2	36.2	40.949	0.9005	6.21	0.4147	.3277	.2893	25.366	774	2957.2	36.2	40.949	0.9005	6.21	0.4147	.3277	.2893
	30.690	1134	3577.7	32.1	38.027	0.8833	7.21	0.3688	.2706	.2297	30.690	1134	3577.7	32.1	38.027	0.8833	7.21	0.3688	.2706	.2297
	32.686	1335	3810.4	29.5	36.933	0.817	7.68	0.3435	.2448	.2065	32.686	1335	3810.4	29.5	36.933	0.817	7.68	0.3435	.2448	.2065
	33.134	1376	3862.6	29.0	36.692	0.8755	7.74	0.3401	.2414	.2029	33.134	1376	3862.6	29.0	36.692	0.8755	7.74	0.3401	.2414	.2029
	36.326	1787	4234.8	23.9	34.935	0.864	8.22	0.3018	.2033	.1693	36.326	1787	4234.8	23.9	34.935	0.864	8.22	0.3018	.2033	.1693
	39.026	2180	4549.5	20.5	33.454	0.856	8.52	0.2773	.1791	.1480	39.026	2180	4549.5	20.5	33.454	0.856	8.52	0.2773	.1791	.1480
	41.133	2460	4795.1	19.0	32.298	0.849	9.05	0.2676	.1668	.1365	41.133	2460	4795.1	19.0	32.298	0.849	9.05	0.2676	.1668	.1365
	42.925	2832	5004.0	18.42	31.315	0.843	10.00	0.2508	.1516	.1236	42.925	2832	5004.0	18.42	31.315	0.843	10.00	0.2508	.1516	.1236
	44.624	3226	5202.0	18.0	30.382	0.837	9.49	0.2359	.1383	.1121	44.624	3226	5202.0	18.0	30.382	0.837	9.49	0.2359	.1383	.1121
	44.557	3214	5194.3	18.0	30.420	0.837	9.42	0.2361	.1386	.1123	44.557	3214	5194.3	18.0	30.420	0.837	9.42	0.2361	.1386	.1123
	46.335	3640	5401.7	17.6	29.445	0.828	9.40	0.2240	.1273	.1022	46.335	3640	5401.7	17.6	29.445	0.828	9.40	0.2240	.1273	.1022

K_1 equals 1000 times the ratio between grams of ammonia per gram of water and the equilibrium pressure of ammonia.

K_2 equals 10 times the ratio between mole fraction of ammonia and the equilibrium pressure of ammonia.

K_3 equals the number of grams of ammonia per litre of solution divided by the equilibrium pressure of ammonia.

Discussion of Results

From Figs. 7, 8, and 9, it is noted that the partial pressure curves of the ammonia are concave to the straight line curve of ideal mixtures, and that the curves tend to approach this line with increasing concentration of ammonia. This approach becomes more marked with increasing temperature. Whether these curves, if continued, would cut the straight line curve, and then become concave to the axis of abscissae (i. e., a negative-positive curve as in the pyridine-water system investigated by Zawidzki)¹ or whether the curve would approach the straight line and become asymptotic to it cannot be foreseen. Yet from analogy with the curves of the partial pressures of water it is very probable that the ammonia curves become asymptotic to the straight line; or, in other words, that in dilute solutions of water in ammonia, the partial pressures of the ammonia would approach those required by Raoult's Law.

From the curves of the partial pressures of the water, it is seen that the straight line is approached as the mole fraction of the water increases. As will be noted by comparison with Table II, the regions, in which flex points appear, correspond to those concentrations in which there is a maximum or minimum contraction in volume. Nothing further can be advanced at present to account for this phenomenon.

Since the vapor pressure of ammonia is so much greater than that of water, the total vapor pressure curve will be that of the ammonia curve, and therefore the ammonia solution will most probably not show a maximum or minimum boiling point, as had already been stated by Konowalow.²

A Theory of the Solution of Gases in Liquids

The fundamental concept of the theory of the solution of gases in liquids, which it is desired to advance, is that first enunciated by Graham³ in his remarkable paper, namely

¹ Zeit. phys. Chem., 55, 129 (1900).

² Ber. deutsch chem. Ges., 17, 1531 (1884).

³ Loc. cit.

that "gases owe their absorption by liquids to their capability of being liquefied and to the affinities of liquids to which they become in this way exposed," and that "solutions of gases in liquids are mixtures of a more volatile with a less volatile liquid." Since the condensation of the gas is regarded as the fundamental phenomenon of its absorption by a liquid, and solutions of gases in liquids are liquid mixtures, the following postulates follow:

1. A gas cannot be dissolved in appreciable quantities above its critical temperature, since above the critical temperature liquefaction is impossible. The fixed gases are dissolved to some extent by water and other liquids, but if absorption coefficients are discarded, and the relative number of gas molecules dissolved by the water molecules considered instead, the exceedingly small quantity becomes apparent. Thus according to v. Antropoff¹ one gram of water absorbs 0.123 cc Xenon reduced to N. T. P., Xenon being the most soluble of the noble gases. In other words, 0.055 of a gram mole of water absorbs 0.055 of a gram mole of Xenon, or one molecule of Xenon for 10,000 molecules of water. It is not true liquefaction that is taking place in such cases, but rather a retention of the Xenon molecule by the attractive forces of numerous water molecules.

2. Since solutions of gases in liquids are to be considered as liquid mixtures, the degree of miscibility of the liquids are of great importance. Thus, since liquid carbon dioxide and liquid sulphur dioxide have only a limited miscibility with water, their gases should dissolve in water to a limited extent, for any liquefied gas separating out could not remain as such except at a partial pressure equal to its vapor tension at that temperature. The relative size and shape of the pores in the liquid would also tend to influence the quantity of gas dissolved. Thus Just² found that the solubility of carbon dioxide in various liquids was greater the smaller the refractive index.

¹ Zeit. Elektrochemie, 25, 269 (1919).

² Zeit. phys. Chem., 37, 343 (1901).

This phenomenon could be explained on the basis of the Clausius-Mossotti formula and the electro-magnetic theory of light, whereby

$$u = \frac{n^2 - 1}{n^2 + 2}$$

in which u is the true space occupied by the molecules and n is the refractive index. Likewise, solubility might be in some way related to a quantity such as "b" of van der Waals.

3. The chemical nature of the gas molecules, such as polarity would likewise influence the degree of solution. This was already recognized by Roscoe and Dittmar¹ in their investigation of the solubilities of ammonia and hydrogen chloride in water. Thus, while they denied Bineau's contention that the constant boiling mixtures of hydrochloric acid were definite compounds, they nevertheless concluded that between water and hydrochloric acid there is an attraction appreciably different from that with other gases. The other inorganic acids forming constant boiling mixtures are also strongly polar substances.

On the basis of the above considerations, the solution of gases in liquids may be classified, as follows:

- I. Solution of gases above their critical temperature.
- II. Solution of gases below their critical temperature.
 - (1) Gases, whose condensates have limited miscibility with water, and which are only limitedly soluble, e. g., CO_2 and SO_2 .
 - (2) Gases, whose condensates are miscible with water in all proportions,
 - (a) Those of strong polarity which form constant boiling mixtures, as HCl , and are extremely soluble.
 - (b) Those whose polarity is not as strong, as NH_3 , which can be driven entirely out of solution.

Patrick and McGavack² in their theoretical discussion of

¹ Loc. cit.

² Jour. Am. Chem. Soc., 42, 946 (1920).

the results obtained in their investigation of the adsorption of sulphur dioxide by silica gel, attacked the problem of adsorption in the following manner. Postulating that when any gas is adsorbed in appreciable quantity, condensation of the gas is actually taking place, the question arises how one can account for the fact that the gas pressures in equilibrium are much lower than the vapor tension of the liquefied gas. These authors on the basis of capillarity advanced the thesis that the lowering of the vapor pressure was due to the fact that the liquid was under a tension or a negative pressure. It is well known that a liquid under a hydrostatic pressure has a greater vapor pressure than when under the pressure of merely its own vapor, and conversely when it is under a tension or negative pressure, one would expect a lowering in the vapor pressure. This tension could be calculated on the basis of the Gibbs' relation

$$\left(\frac{dp}{dP}\right)_\tau = \frac{V}{v},$$

in which dp equals the change in vapor pressure, dP equals change in hydrostatic pressure, V equals volume of condensed liquid phase, and v equals volume of the gas. Furthermore, this tension must cause a dilation of the liquefied gas to an extent that is proportional to the compressibility of the liquid. The compressibility of the liquid was taken as some function of the surface tension. They finally developed the following formula which tallied very well with experimental results:

$$V = K \left(\frac{P\sigma}{P_0} \right)^{\frac{1}{n}}$$

1 which V is the volume of the condensed gas absorbed per gram of gel; i. e., the mass of the gas adsorbed divided by the density of the liquefied gas at the temperature; P is the equilibrium gas pressure; σ is the surface tension and P_0 the vapor tension of the liquefied gas at the temperature. K and $1/n$ are constants. By plotting the values of $\log V$ as ordinates and $\log \frac{P\sigma}{P_0}$ — as abscissae, the experimental values of Patrick and McGavack fell on a straight line.

Since the solution of gases in liquids is also considered as a condensation, the results obtained in this investigation were also plotted according to this formula as can be noted from Fig. 10. The densities and values of the surface tension

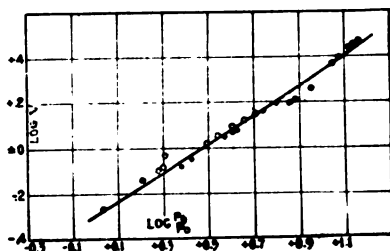


Fig. 10

Solubility of NH_3 in H_2O . \circ at 0°C ;
 \circ at 20°C ; \bullet at 40°C

of liquid ammonia at 0°C , 20°C , and 40°C , were interpolated from the values of Berthoud¹ and the vapor tensions used were those obtained at the Bureau of Standards.² The results obtained for 0°C , 20°C , and 40°C , with solubilities ranging from 0.315 gram to 1.885 grams of ammonia

per gram of water are so well represented by this formula, that it may be assumed that a phenomenon similar in its manifestations to that of the adsorption of sulphur dioxide by silica gel is occurring in the case of the solution of ammonia in water.

In Curve I, Fig. 11, other available data on the solubility of ammonia in water at lower pressures obtained by Perman, Roscoe and Dittmar, and Sims, at 0°C , 20°C , and 40°C and by Mallet³ for pressures of 743 to 744.5 mm, at -10°C , -20°C , -30°C , and -40°C , as well as the results obtained in this investigation were plotted. The results obtained in this investigation as well as by other investigators at varied temperatures and pressures, and concentrations as high as 2.746 grams ammonia per gram of water fall on the same straight line curve. This is apparently a general law for the solution of ammonia in water.

On Curve II, same figure, have been plotted in like manner the solubility of hydrogen chloride in water as found by Roscoe and Dittmar⁴ at 0°C , and pressures varying from 58 to 1270

¹ *Helv. Chim. Acta*, **I**, 84-7 (1918); *Jour. Chim. phys.* **16**, 429 (1918).

² *Jour. Am. Chem. Soc.*, **42**, 206 (1920).

³ *Am. Chem. Jour.*, **19**, 804 (1897).

⁴ *Loc. cit*

mm. The surface tension of liquid hydrogen chloride was calculated from the work of McIntosh & Steel¹ to be 7.6 dynes; the density of liquid hydrogen chloride was taken as 0.908 according to Ansdall;² and vapor tension of liquid hydrogen chloride was taken as 19,900 mm according to Faraday.³

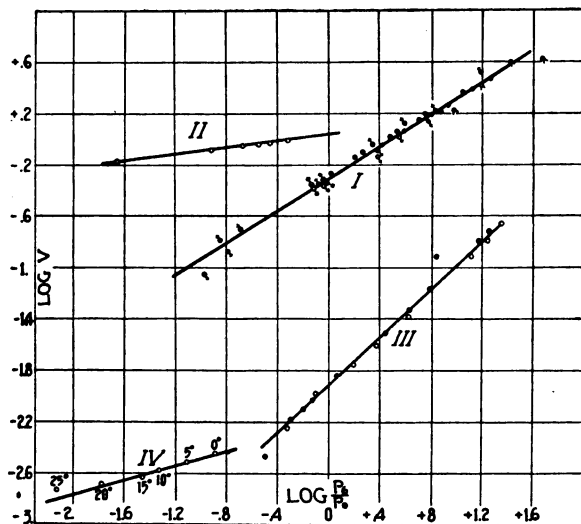


Fig. 11

On Curve I ○ indicates observations at 0° C; ● at 20° C; ◐ at 40° C. † appended indicates data of Sims; ‡ data of Perman; and R data of Mallet. On Curve III ○ indicates data at 7° C and ● data at 20° C

On Curve III, there has been plotted the solubility of sulphur dioxide in water, as found by Sims⁴ at 7° C from pressures of 27 to 1291 mm, and at 20° C, from 32.4 to 1911 mm. The values of the surface tension of liquid sulphur dioxide at 7° C and 20° C were calculated from values given by Landolt-Börnstein to be 27.2 and 24.5 dynes, respectively.

¹ Zeit. phys. Chem., **55**, 141 (1906).

² Proc. Roy. Soc., **30**, 117.

³ Phil. Trans., **135**, I, 155 (1845).

⁴ Loc. cit.

The density of liquid sulphur dioxide was interpolated from the data of Cailletet and Matthias¹ and taken as 1.383 for 20° C, and 1.42 for 7° C. Regnault's values for the vapor tensions were used.²

On Curve IV, was plotted the solubility of carbon dioxide in water at 760 mm pressure at from 0° C to 25° C. The solubility data were those of Bohr and Bock.³ The values of surface tension at these temperatures were obtained by interpolation from data given by Landolt-Börnstein, the values used being as follows;

Temperature, C	0	5	10	15	20	25
Surface Tension	4.65	3.5	2.74	1.82	1.00	.50 dynes

The density of liquid carbon dioxide at these temperatures was obtained from the data of Warburg and v. Babo.⁴ The data of Th. Tate⁵ on the vapor tension of liquid carbon dioxide were used.

From the Curves I to IV it is evident that for each individual gas the law contained in the formula

$$V = K \left(\frac{P_{\sigma}}{P_0} \right)^{\frac{1}{n}}$$

holds very well, but that these lines do not coincide. From a consideration of the nature of the solution of gases in liquids such as outlined above no such coincidence would be expected. If this formula is written in logarithmic form, there is obtained the following equation:

$$\log V = \log K + \frac{1}{n} \log \frac{P_{\sigma}}{P_0}$$

In the above equation when $\frac{P_{\sigma}}{P_0}$ is set equal to 1, log K becomes

¹ Comptes rendus, **104**, 1565 (1887).

² Landolt-Börnstein Tabellen.

³ Wied. Ann., **44**, 318 (1891).

⁴ Ber. Berl. Akad., p. 509 (1882).

⁵ Phil. Mag., (4), **26**, 502.

equal to $\log V$. $1/n$ is obviously the slope of the straight line. If solutions of gases in liquids are considered as binary mixtures, it is evident that for the same solvent, those gases which in the liquefied state mix in all proportions with water (an indication that their molecular forms are such that the molecules of the one liquid fit into the pores of the other liquid) their condensates will be taken up in greater quantity than those of gases whose condensates have only a limited miscibility with water. Besides the degree of miscibility, such factors as the dielectric constant of the liquefied gas (which is a function of the space occupied by the molecules), no doubt play an important rôle in determining the degree of solubility. It is proposed that the values of the constants K and $1/n$ depend on such factors as miscibility and dielectric constants of the liquefied gases, etc. In fact from a comparison with Fig. 11 it becomes evident that K is much greater for the solubility curves of ammonia and hydrogen chloride, which in the liquid state are miscible with water in all proportions than for carbon dioxide or sulphur dioxide whose condensates have only a limited solubility in water. Also, in the case of these four gases, it has been found that the values of $1/n$ parallel to some extent the values of the dielectric constant of the liquefied gas dissolved, i. e., those gases whose liquids possess a high dielectric constant have a large value of $1/n$. But unfortunately, there are not enough data available for other gases to test out the validity of this relation.

However, this fact is worthy of note—that the values of K and $1/n$ for each particular gas are independent of the temperature and the partial pressure of the dissolved gas. This fact is of great importance; and, though only speculation as to its significance is possible at present, it offers very fertile fields for investigation as to the factors on which the values of these constants depend in the application of the adsorption formula to the case of the solubility of gases in liquids.

Summary

- (1) A static method has been developed for measuring

the partial pressure of a component which is relatively very small compared to the partial pressure of the second component.

(2) This method has been used to determine the partial pressures of water and ammonia of concentrated ammonia solutions at 0° C, 20° C, and 40° C, at partial pressures of ammonia varying from 1000 to 4000 mm. The partial pressures of the ammonia were measured to within 4 to 2 millimetres; and those of the water to 0.08 millimetre.

(3) The solubility of ammonia in water was determined at 0° C, 20° C, and 40° C at pressures from 750 to 3600 mm. The densities of these solutions were also determined.

(4) A theory of the nature of solutions of gases in liquids first advanced by Graham, has been amplified, and solutions of various gases in liquids classified on the basis of some of the physical and chemical properties of the gas.

(5) The formula

$$V = K \left(\frac{P\sigma}{P_0} \right)^{\frac{1}{n}}$$

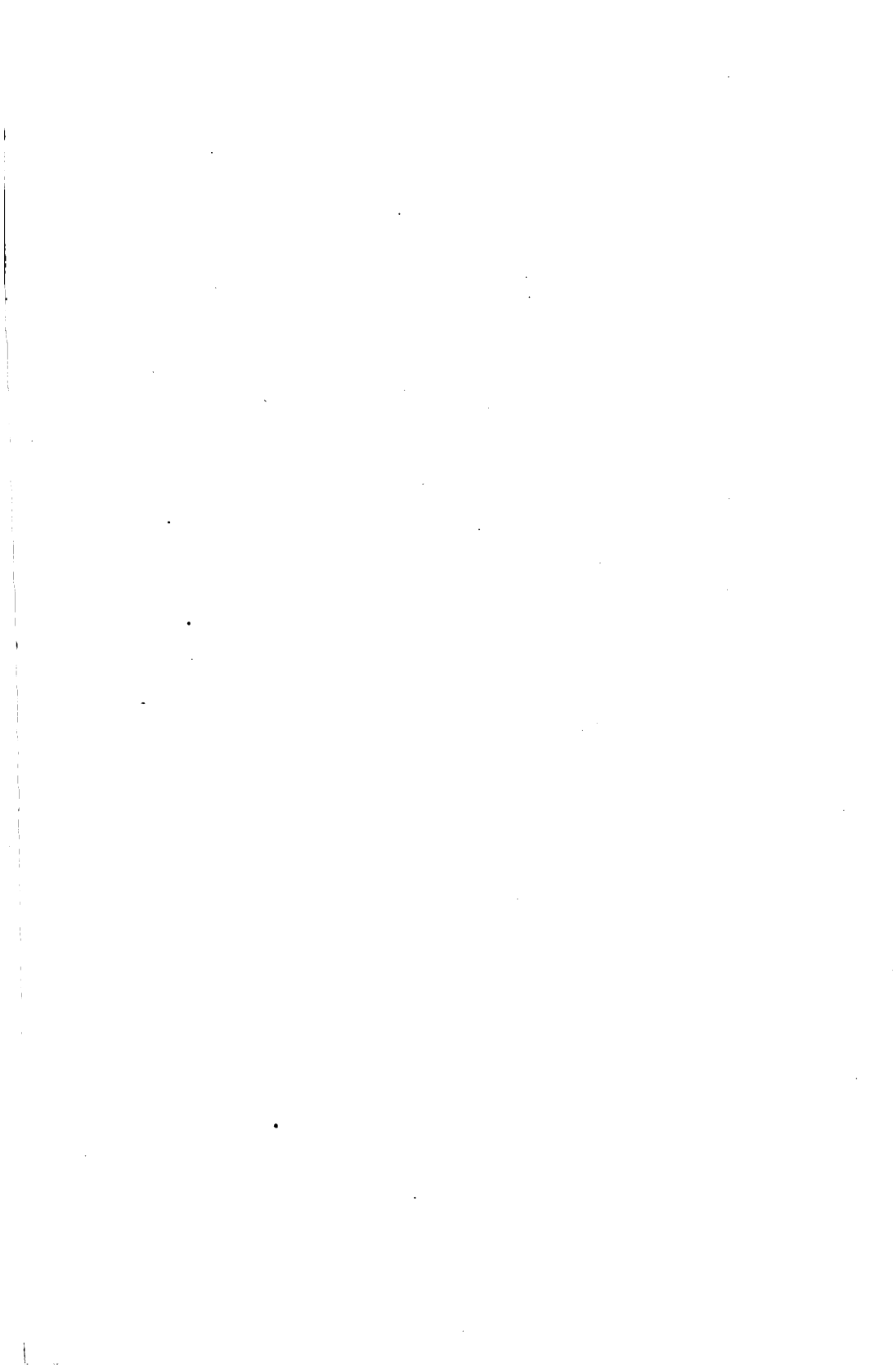
has been found to represent well the solubility of ammonia hydrogen chloride, sulphur dioxide, and carbon dioxide in water at varied temperatures and pressures. In this formula V is the volume occupied by the liquefied gas dissolved per gram of water; P_0 is the vapor tension and σ the surface tension of the liquefied gas at the temperature while P is the equilibrium gas pressure. The constant K for ammonia has the value 0.49 and $1/n$ has the value 0.69.

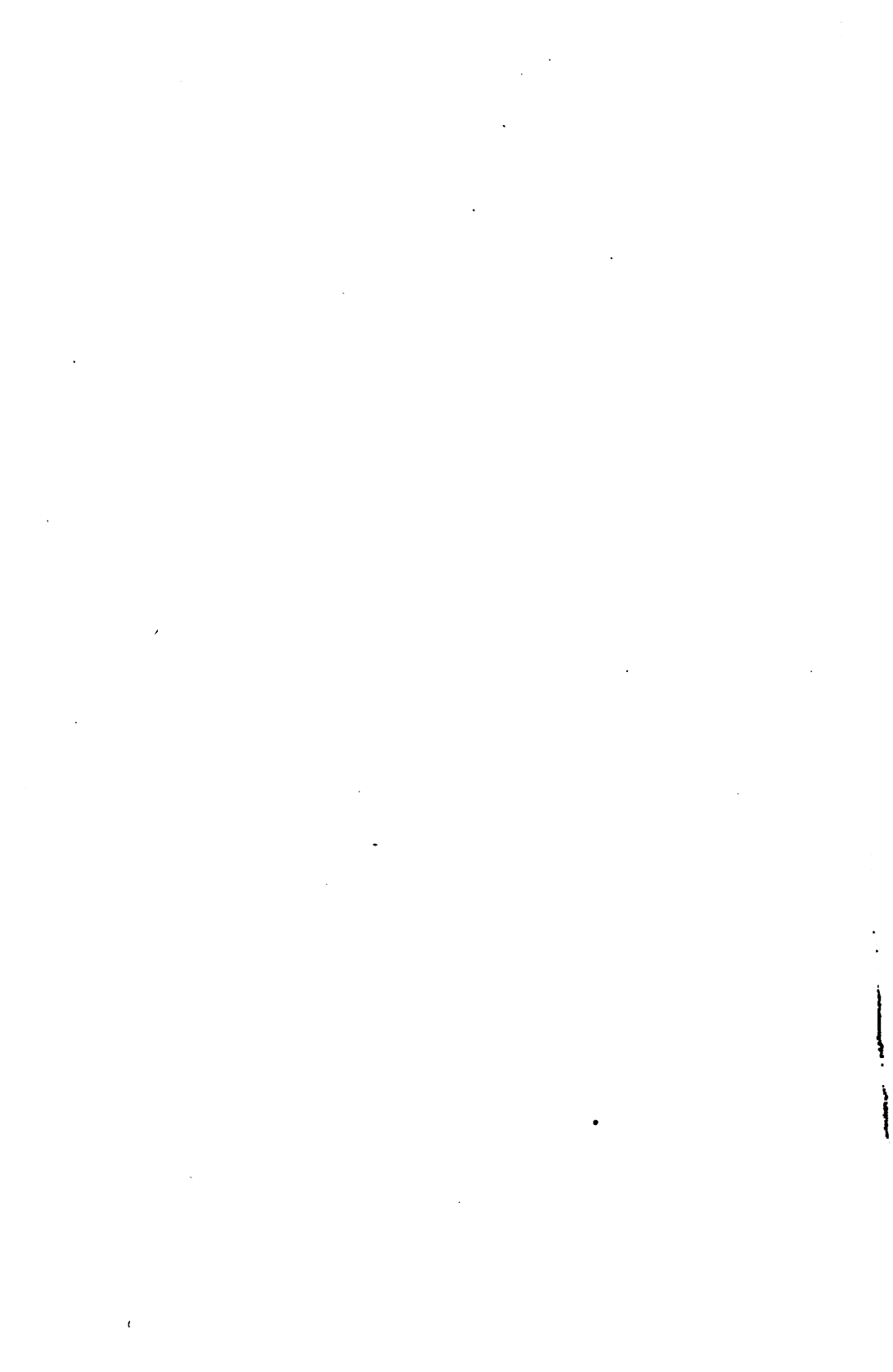
(6) Solubility data of HCl , SO_2 , and CO_2 have also been plotted according to this formula.

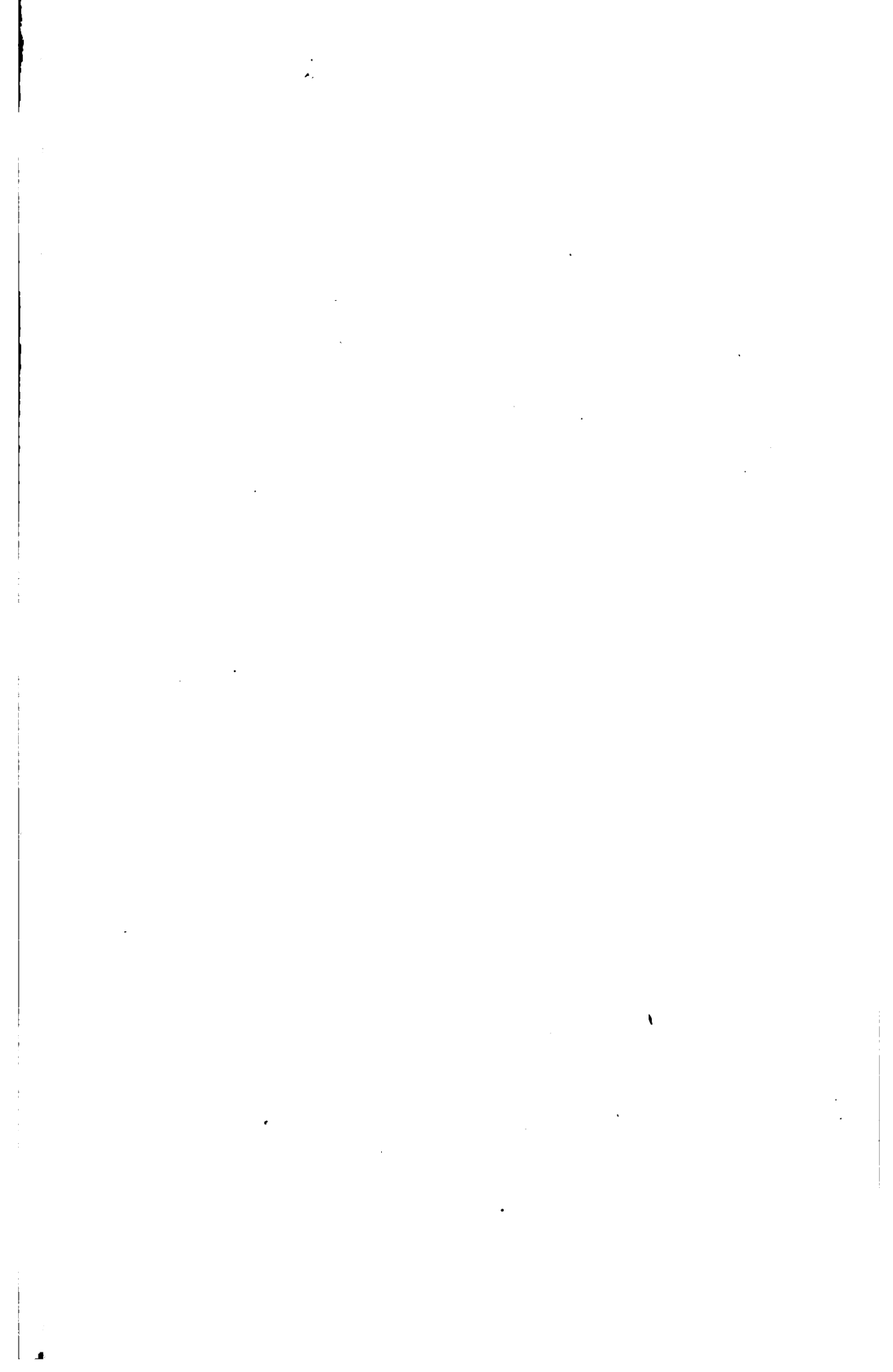
BIOGRAPHY

Benjamin Simon Neuhausen was born July 31, 1896. His early education was received in the public and high schools of New York City. In 1918 he received the A. B. degree from Johns Hopkins University. During the year 1919-1920 he was a Hopkins Scholar and Student Assistant; during 1920-1921 he was a Du Pont Fellow.

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